Computer and Information Science
Materials Modeling

Toward Computational Atomic-Scale Design and the Predictive Engineering of Materials
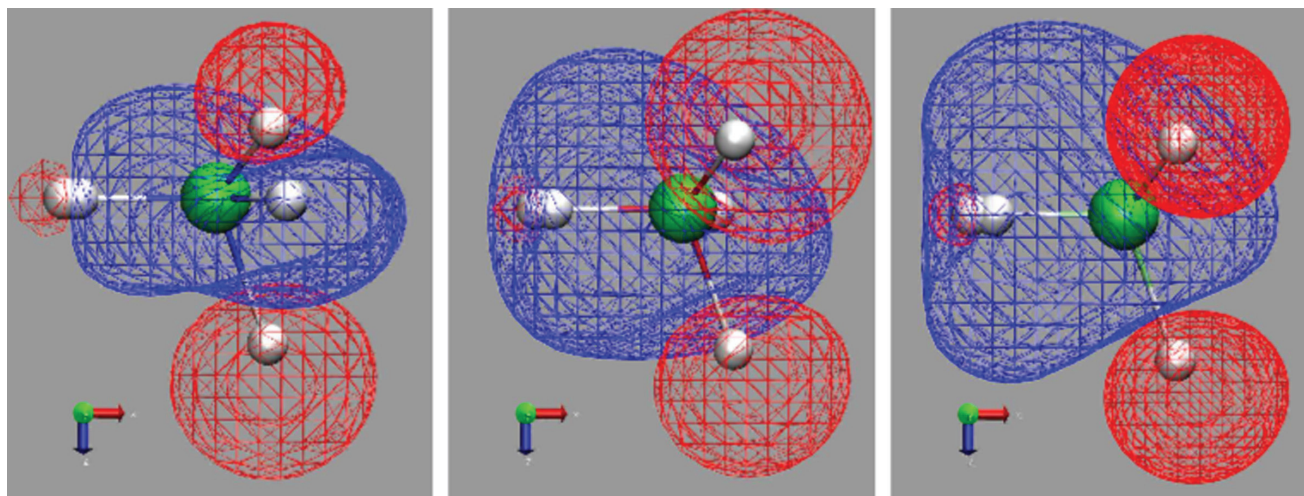

Figure 1: Differences in external potentials for superimposed compound pairs NH_3/CH_4, H_2O/CH_4, and HF/CH_4 (left to right). Blue and red represent positive and negative isovalue surfaces, respectively.

Researchers are exploring the purposeful design of compounds with optimized properties.

For more information:

Technical Contacts:
O. Anatole von Lilienfeld
505-284-8829
oavonli@sandia.gov

Science Matters Contact:
Alan Burns
505-844-9642
aburns@sandia.gov

Systematic approaches towards the virtual engineering of chemical composition, attempting to computationally identify compound candidates that meet sets of specific desired property requirements, is a worthwhile goal in general, and for pharmaceutical and materials research in particular. Ideally, quantitative structure property relationships (QSPR) can be identified, and used for numerical screening or within optimization algorithms. The eventual goal being, to answer the ``inverse'' question: under specified conditions, which compound will exhibit a certain desired property?

The concept of Chemical Compound Space (CCS) has recently received increased attention in the computational physical, chemical, biomolecular and atomistic materials sciences in the context of its exploration for the purposeful design of compounds with optimized properties. CCS, the combinatorial set that encompasses all stable chemical compounds, provides a rigorous framework in which to construct the mathematical tools for the development of physical chemistry-based direct and inverse QSPRs. One can view CCS as the high dimensional set populated by all the possible combinations (stoichiometries) and configurations (isomers) of elementary particles that make up electronic and nuclear densities. Due to the large cardinal number of CCS, simple enumeration is computationally prohibitive. For example, alkanes (a relatively simple class of molecules) with up to 80 carbon atoms are estimated to include more than 10^{28} topological isomers. Consequently, listing the corresponding molecular topologies becomes practically impossible, let alone attempts to screen. In general, the *de novo* design of interesting material is very likely to be tackled inefficiently by screening methods. This is not only because CCS is astronomically large but also because the chances to "stumble" across a "hit" decrease exponentially with the number of

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material properties (if uncorrelated) that must be exhibited simultaneously.

   This inefficient state of affairs has motivated the development of more "rational" first principles design methodologies that usually rely on electronic-structure methods because composition, and thereby chemical bonding, must be varied frequently and freely. In order to optimize electronic eigenvalues (ε) of materials (a central property relevant to photo-voltaic, battery, or catalysis applications) "alchemical" gradients in CCS have been developed that measure the response of ε to changes when the computational model of compound i is continuously transformed into the computational model of compound j, driven by an order parameter (λ). Such gradients could form the future basis for gradient-based optimization algorithms that generally offer drastically improved performance.

   If both compounds have the same number of electrons, research at Sandia has shown that the gradient of their electronic potential energy (E) is the quantum mechanical expectation value of the difference of their corresponding Hamiltonians (H). Within the electronic structure method Density Functional Theory, this expectation value is tantamount to the integral over the product of electron density (n) and the difference in external potentials (v):

$$\frac{dE(\lambda)}{d\lambda} = \langle H_j - H_i \rangle_\lambda = \int d\mathbf{r} n_\lambda(\mathbf{r}) \cdot [v_j(\mathbf{r}) - v_i(\mathbf{r})]$$

   Figure 1 features differences in external potentials for three exemplary isolated compound pairs: NH_3/CH_4, H_2O/CH_4, and HF/CH_4. Figure 2 illustrates the ε-property as a function of λ (symbols) and predictions of CH_4's ε-property made using gradients at NH_3, H_2O, or HF (solid arrows). These predictions deviate substantially from the ideal predictions (pink) that would be useful for gradient-based optimization algorithms. Based on an empirical scheme, corrected predictions have been developed that promise higher accuracy (dotted arrows). The next step will be to tie these gradients into gradient-based optimization algorithms of materials properties.

Reference:

"Accurate ab initio energy gradients in chemical compound space" O. Anatole von Lilienfeld, *J. Chem. Phys.* **131** 164102 (2009)
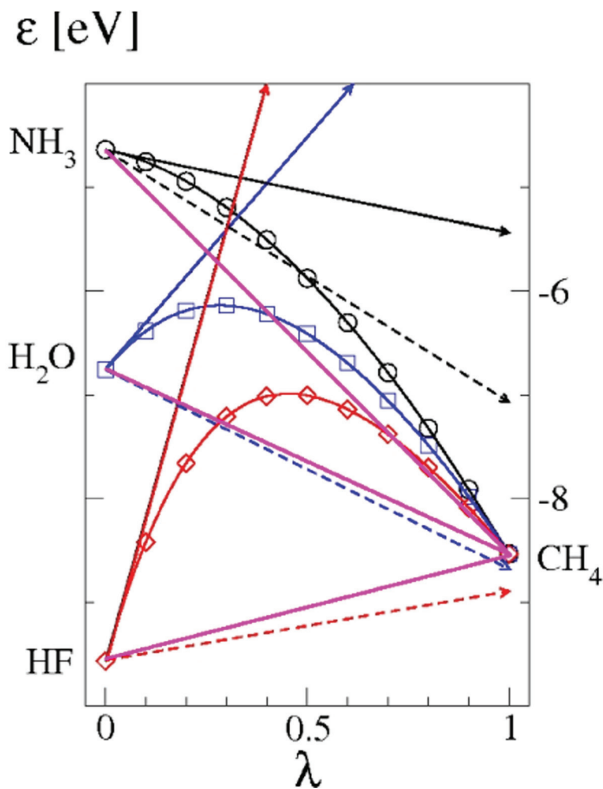

Figure 2: : ε-property as a function of λ (symbols), and predictions of CH_4's ε-property made using gradients at NH_3, H_2O, or HF (arrows). Pink lines correspond to perfect predictions.